Krypton Physisorption for Characterization of Nanoscopic Microporous Thin Films

Volumetric physisorption analysis is typically conducted using sample amounts of the order of 20 milligrams to a few grams. For smaller sample quantities and for extremely low surface area samples, the number of non-adsorbed gas molecules at adsorption equilibrium can exceed the amount of molecules adsorbed on the sample, which will hamper the accurate measurement of gas uptake by the sample. Because of this effect the typical surface area detection limit for nitrogen physisorption at 77 K is assumed to be about 1 m^2. This detection limit may be significantly reduced by using krypton adsorption analysis at the same temperature that for krypton is below its triple point and where its saturation pressure is 2.32 mbar i.e. ~430 times lower than psat of N2. It follows that at any given relative gas pressure the absolute pressure of krypton is 430 times lower than that of nitrogen. This also means that the density of krypton in the free space is proportionally lower, which leads to the significant improvement of detection limit for krypton.

Krypton physisorption was recently applied for the characterization of nanoscale films of the first microporous material deposited by vapor deposition.[1] The microporous metal-organic framework (MOF) thin films were conformally deposited on the nanofabricated high-aspect-ratio silicon micropillar arrays to increase the thin film quantity per sample for the measurement, while maintaining the nanoscopic thickness of the films (Fig. 1).

An accurate pore size analysis of these 100 nm thin films was conducted using krypton physisorption using a high-resolution Micromeritics 3Flex adsorption instrument. The 3Flex was equipped with high-vacuum system with three micropore-capable ports.

The adsorption isotherm plotted in Fig. 2 in a semi-log scale is a representative example of krypton adsorption isotherms measured in this study. The relative pressure of a sharp step observed in the low relative pressure range is consistent with the predicted condensation pressure of krypton in the pores of this crystalline MOF material.

Note that the gas uptake intervals of the isotherm account to merely 1 µl of krypton at STP. This resolution is enabled by the high-accuracy and low-pressure readout of the 3Flex instrument, in combination with the shift of the isotherm to low pressures enforced by the use of krypton instead of nitrogen. The amount of krypton in free space is nearly negligible in comparison to the amount of nitrogen or argon that would be present at same relative pressures.

The Brunauer–Emmett–Teller (BET) method was applied to calculate the specific surface area of the sample (Fig. 3). Taking into account the 'type I' shape of the isotherm, a linearization in a relatively low relative pressure range (0.005-0.05) was used. The suitability of this pressure range was verified in the MicroActive software by monitoring of the Rouquerol transform

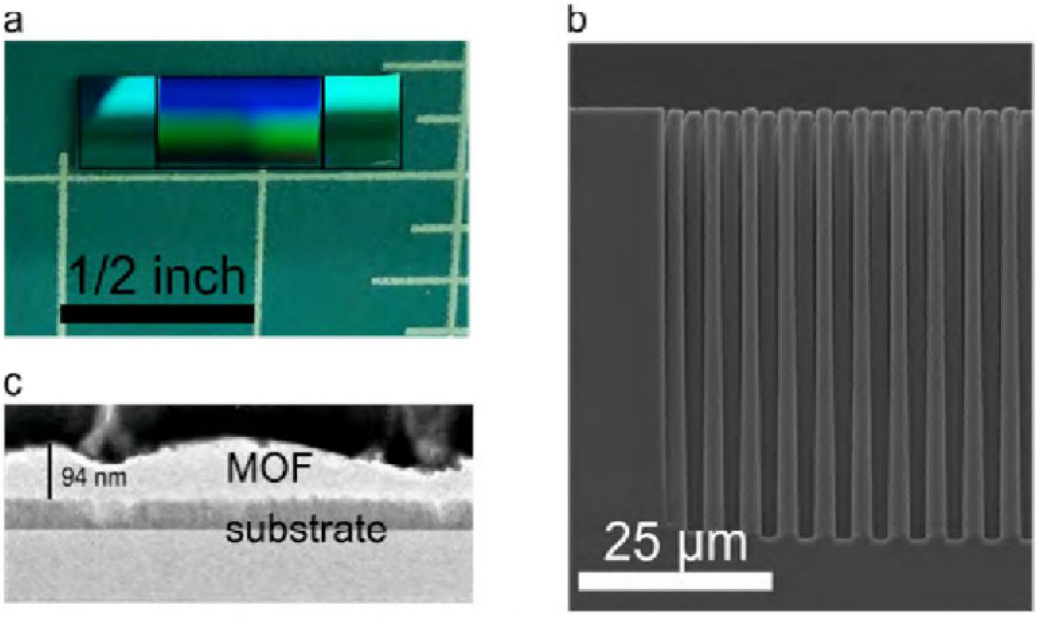

Fig. 1 Conformally deposited MOF films on high aspect ratio micropillar array. (a) Photograph of the coated array. (b) SEM cross sectional image of the coated array. (c) TEM high resolution cross sectional image of the MOF film.

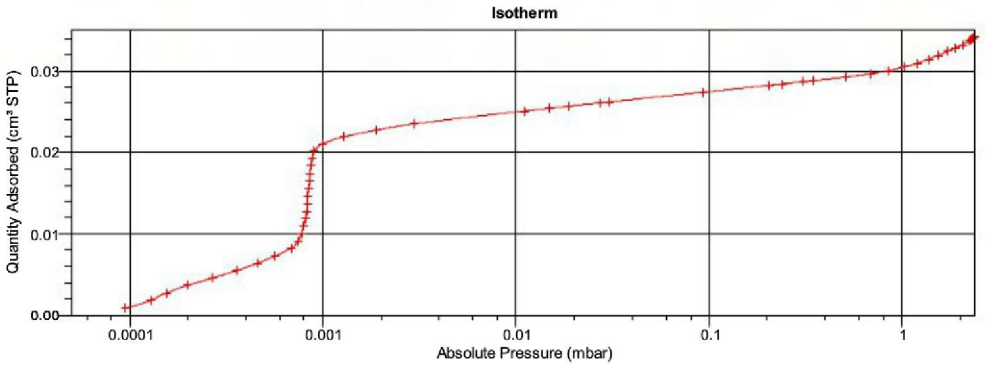

Fig. 2 Krypton adsorption isotherm measured on a 100 nm MOF film at 77 K.

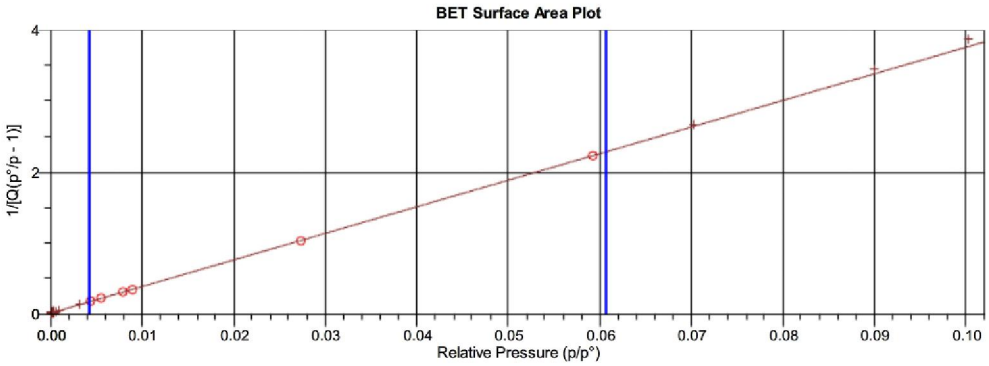

Fig. 3 BET plot of the example krypton isotherm.

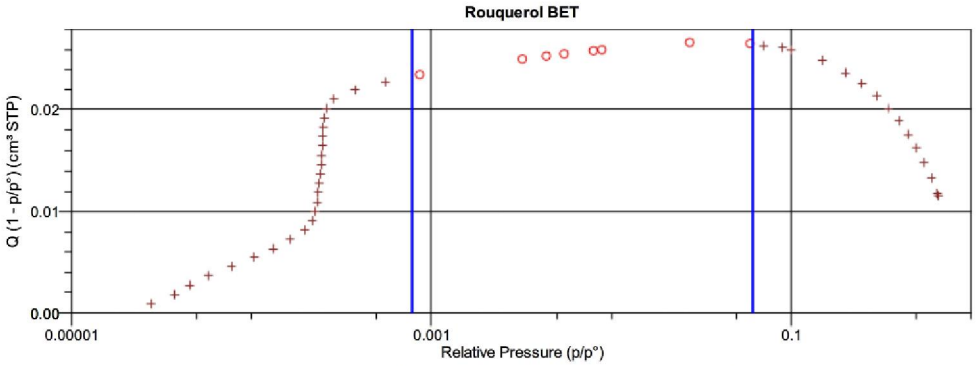

Fig. 4 Rouquerol parameter plot calculated for the isotherm in Fig. 2.

(Fig. 4). This parameter should not decrease in the range selected for linearization of the BET transform.

The BET specific surface area calculated from krypton adsorption isotherm presented in Fig. 3 was 0.15 m². This value was matched to a computational approximation of the surface area based on the crystal structure and to experimental reference measurements, to directly assess the quality of the microporous material in the nanoscopic film. Optical measurement of the film area was used to quantify the area-normalized BET specific surface area of the film. Due to the sensitivity of the measurement, 'background 'surface areas such as that of the sample tube and substrate might interfere with the result (leading to an error of a few % in the example). For this reason, the isotherm of a non-coated sample was measured in the same tube and the BET of the sample was corrected for this contribution. Using this method, average film thickness approximations could be calculated from the isotherms of different films, which corresponded well with the thicknesses measured by electron microscopy.

1. I. Stassen, M. Styles, G. Grenci, H. V. Gorp, W. Vanderlinden, S. D. Feyter, P. Falcaro, D. D. Vos, P. Vereecken, R. Ameloot, Nat. Mater. 2015, DOI 10.1038/nmat4509.